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CHEMICAL AND LOCALIZATION EFFECTS IN AUGER LINESHAPES OF TRANSITION METAL COMPOUNDS

By

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The compounds MX_n (X=C, N, O) display sequential changes in the C-KLL Auger spectra and these changes correlate with the density-of-states (DOS), the relative proportions of ionic, covalent and metallic bonding, and screening and localization of the Auger holes. In this work we quantitatively interpreted the C-KLL lineshape of TiC, using previously described techniques. We further investigated the X-KLL lineshape changes as the number of 3d electrons increases across the rows of the transition metals, and as the nonmetalloid atom changes from C to N to O. The effects of sample nonstoichiometry were also examined.

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CHEMICAL AND LOCALIZATION EFFECTS IN THE AUGER LINESHAPES OF TRANSITION METAL COMPOUNDS

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The compounds MX_m (X=C,N,O) display sequential changes in the C-KLL Auger spectra(1), and these changes correlate with the density-of-states(DOS), the relative proportions of ionic, covalent and metallic bonding, and screening and localization of the Auger holes. In this work we quantitatively interpreted the C-KLL lineshape of TiC, using previously described techniques.(2) We further investigated the X-KLL lineshape changes as the number of 3d electrons increases across the rows of the transition metals, and as the nonmetalloid atom changes from C to N to O. The effects of sample nonstoichiometry were also examined.

The carbon-based DOS of the carbides is composed of three regions: the approximately atomic-like C2s electrons at 10-12 eV, the C2p electrons at roughly 3-7 eV sigma-bonded with the metal 3d-eg metal orbitals, and the C2p electrons at 0-3 eV pi-bonded to the metal 3d-t2g orbitals. The 2s electrons are nonbonding and relatively localized on the carbon nucleus. The covalent sigma-bonded C2p electrons contribute to MO's with much of their density located interatomically between the carbon and metal nuclei. The higher electronegativity of N or O makes the bond more ionic, resulting in less electron density in the inter-atomic region, and more density localized on the nuclei. The C2p-pi electrons contribute to the comparatively delocalized MO's largely responsible for the metallic conductivity shown by many of these compounds.

The C-K_α spectra (which samples the C2p DOS) of the metallic carbides develop a feature on the high energy side of the main peak as the number of 3d-t2g electrons increases.(3) The band calculations of Neckel et.al.,(4) show that the intensity of the metallic unoccupied-DOS (primarily t2g) increases with separation from the Fermi level. Since the C2p orbitals

contribute to the band containing the metallic electrons, the [illegible]f the high energy feature in the C-XES spectrum increases proportionally as metal 3d electrons fill the t2g states. There is controversy about the nature of the XES high-energy feature, viz., whether it originates via a molecular orbital or from an interatomic transition. In view of the relatively small transition matrix elements of the latter, the molecular orbital interpretation is preferred.

In the limit of the one-electron approximation, (i.e. assuming the holes are completely delocalized and do not interact) the KLL Auger spectrum as given by the fold of the valence band DOS, consists of 3 peaks corresponding to transitions involving ss, sp and pp electrons. It is the fold of the C2p-Π states with the more numerous C2p states which produces the high energy feature characteristic of the C-KLL Auger spectra of the carbides, and of the MX_n compounds in general. As the density of the metal 3d electrons increases so does the intensity of the high energy feature. A second feature which changes with the number of metal 3d electrons is the sp peak. This peak reflects the magnitude of multiplet (singlet-triplet) splitting, which is a very sensitive measure of the hole-hole interaction. The splitting decreases as the number of mobile, screening 3d-t2g electrons increases.

Finally, the shifting of the peaks from the energies predicted in the one-electron limit reflects the effects of increasing localization, as the metal-nonmetal electronegativity difference increases, and as the number of metal 3d electrons decreases. In fact, the pp Auger peak and the high energy shoulder show little if any deviation from the values predicted for the one-electron model, even for the relatively ionic carbides, e.g. TiC. However, the ss and sp peaks are still clearly affected by localization, as evidenced by their substantial downward energy shift from the one-electron fold and marked sp multiplet splitting.

These trends are even more noticeable when the nonmetalloid atom is changed from C to N to O. The large changes in the electronegativity

difference between the metal and nonmetal atom again correlate with the changes in localization and multiplet splitting. In addition, the separation of the high energy feature from the main pp peak increases, while the intensity of the feature diminishes. Examination of the DOS of the compounds can explain these phenomena without invoking localization. The main C2p peak and the Fermi level are separated by the high energy wing comprised of the pi-bonded C2p states. As the bond ionicity increases from C to N to O, the main X-2p peak narrows and is pulled down from the Fermi level. The metal 3d-eg orbitals and the X-2p level become increasingly separated, reducing the energetic overlap between them. As a result, the electron density which was once interatomically located in the covalent bond is redistributed to the X atom and the 3d-t2g metal MO, effectively raising the Fermi level, and extending the high energy wing, to give a higher-energy but lower-intensity mean p-pi DOS This is reflected in the X-KLL Auger spectrum as a simultaneous increase in the separation and decrease in the intensity of the high energy feature with respect to the main pp peak. In some cases, e.g. TiC, the high energy states are largely unoccupied, since the Fermi level falls on the upper shoulder of the main C2p peak in the XES spectrum.

It has been demonstrated (5) that in the series TiO, TiN, TiC the local excitation threshold (measured as the intersection of the emission and absorption thresholds for the Ti2p hole) is increasingly different than the Fermi level (as measured from the Ti2p XPS line). This difference reflects the effectiveness of the metallic electrons in screening the Ti2p core hole and therefore indicates that screening of the Ti hole is most effective in the oxide, consistent with the increase in the number of metallic electrons in the t2g orbitals. However, the X-KLL Auger lineshapes of the same series reveal increased multiplet splitting and localization effects in the oxide, compared to the carbide, indicating reduced screening of the O-pp and ss valence holes. The two types of holes are clearly influenced in different fashion by the amount of interatomic vs. metallic charge.

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